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Local singlet for CuO and Nd_2CuO_4

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Photoemission $3d$ spectra according to the Anderson impurity model and experiment are compared for CuO and Nd_2CuO_4. While good agreement between theory and experiment is obtained for CuO, the calculated local singlet has much more weight than observed for Nd_2CuO_4. This suggests an appreciable difference between the low-energy excitations in CuO and Nd_2CuO_4, which is surprising due to the similarities of the compounds, both having formally divalent Cu coordinated to four oxygen atoms in an approximate square. This difference is not predicted by the impurity Anderson model.

It is often assumed that essential aspects of the electronic structure of high-T_c superconductors can be described by models which include the Cu $3d$ and O $2p$ orbitals in the CuO planes. This leads to a picture where the low-lying excitations are described in terms of a so-called local singlet,[1] consisting of a $3d$ hole coupling to an O $2p$ hole on the surrounding four O atoms forming a state with $^1A_1$ symmetry with respect to the Cu site. This local singlet is expected to be seen in, for instance, photoemission electron spectroscopy (PES). This has been studied theoretically using the Anderson impurity model,[2-4] and in extended Hubbard models.[5,6] All these calculations show a sizable peak of local singlet character at low binding energy. Experimentally, however, very little weight or no weight at all is seen at the corresponding energies for the high-T_c-related compounds. In this context it is interesting to study CuO, which like the undoped High-T_c-related compounds, has formally divalent Cu coordinated to four O atoms in an approximately quadratic arrangement. We note, however, that CuO and Nd_2CuO_4 are quite different in terms of the long-range geometry of the Cu and O atoms, as discussed at the end of this paper. The aim of this paper is to compare theoretical and experimental results for CuO and the high-T_c-related compound Nd_2CuO_4.

PES spectra of CuO have earlier been studied experimentally by Thuler, Berbow, and Hurych,[7] Ghijsen and co-workers,[8,9] and Shen *et al.*,[10] and theoretically by Eskes, Tjeng, and Sawatzky[11] and Ghijsen *et al.*,[8] who used a cluster model. Here we use the Anderson impurity model, which includes one Cu impurity interacting with a surrounding host:

$$H_0 = \sum_{\mathbf{k},\sigma} \varepsilon_{\mathbf{k}} n_{\mathbf{k}\sigma} + \sum_{m,\sigma} \varepsilon_m n_{m\sigma} + \sum_{\mathbf{k},m,\sigma} (V_{\mathbf{k}m} \psi^\dagger_{\mathbf{k}\sigma} \psi_{m\sigma} + \text{H.c.}) + \sum_{i<j,r<t} U_{ijrt} \psi^\dagger_j \psi^\dagger_i \psi_r \psi_t, \quad (1)$$

where ε_m are the energies of the $3d$ electrons on the impurity site, with the orbital label m and the spin σ. The other valence electrons are described by $\varepsilon_{\mathbf{k}}$, and the hopping between these states is given by $V_{\mathbf{k}m}$. The Coulomb interaction between the $3d$ electrons is given by the last term, where i stands for $(m\sigma)$. This term includes multiplet effects for the d^8 configuration. The parameters are obtained as described earlier,[4,12] i.e., all parameters are obtained from *ab initio* calculations, except the ones describing the multiplet splittings, which are obtained from atomic data.[13] The oxygen-oxygen hopping as well as hopping to Nd (for Nd_2CuO_4) is included in the values of $\varepsilon_{\mathbf{k}}$ and $V_{\mathbf{k}m}$. The method for calculating the spectra is in the spirit of earlier work for Ce,[14] but includes multiplet effects. The method has been described briefly elsewhere.[4] Only the emission from the Cu $3d$ level is considered. The ground state is assumed to have x^2-y^2 symmetry relative to the Cu atom. As in previous work,[8,11,4] the calculation neglects all configurations including conduction electrons, since these are higher in energy due to the band gap. The accuracy of this approximation has not been tested.

The results for CuO are shown in Fig. 1, and compared with the high-resolution x-ray photoemission spectroscopy (XPS) data by Shen *et al.*[10] The main band at about -5 eV to -1 eV, corresponds to states of mainly d^9L^{-1} character, where L^{-1} stands for a ligand (O $2p$) hole. This peak is in rather good agreement with the experimental results. The satellites at -10, -12, and -17 eV correspond to states of mainly d^8 character, which are split by multiplet effects. They appear at somewhat larger binding energies than is seen experimentally. This could be due to a somewhat too large value for the Coulomb interaction U between two $3d$ electrons, which was actually calculated for La_2CuO_4.[15] The theoretical peak at about 0.3 eV corresponds to the local singlet. This peak results from the interaction of the d^9L^{-1} states with d^8 and $d^{10}L^{-2}$ states via the hopping matrix elements, which causes a bound state to be split off from

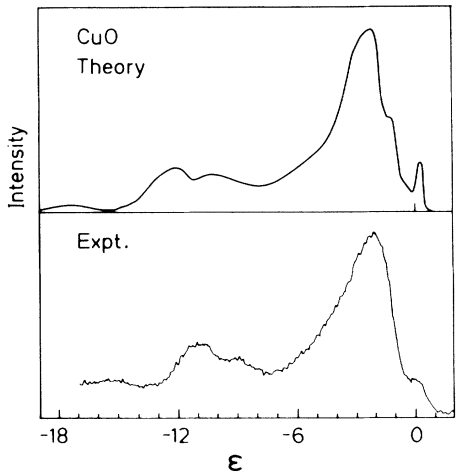

FIG. 1. Theoretical and experimental PES spectra for CuO. A Gaussian broadening of 0.25 eV (full width at half maximum) was used to simulate the experimental broadening. Energies are in eV. The experimental results are from Shen *et al.* (Ref. 10).

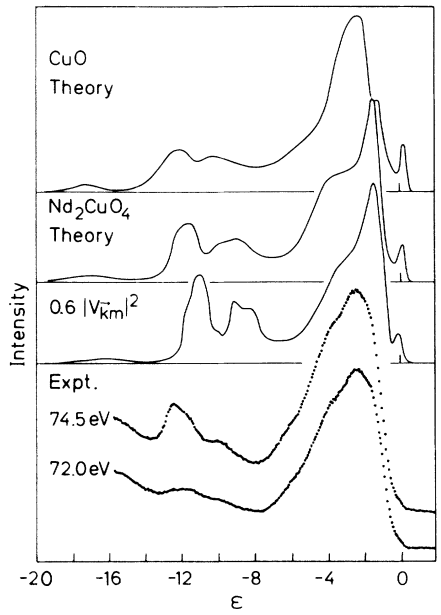

FIG. 2. Comparison of theoretical results for CuO (top) and Nd_2CuO_4 (second from top). We also show results for Nd_2CuO_4 when $|V_{km}|^2$ has been reduced by a factor 0.6 (third from top). The two bottom curves show experimental results for Nd_2CuO_4 taken at two photon energies. The experimental results are from Ref. 4. Energies are in eV.

the main band. Experimentally, a shoulder is seen at the same energy as the theoretical local singlet, although the experimental structure is much broader than the calculated one. This may be due to our use of an impurity model in the theoretical description. For a lattice model, one may expect broadening effects due to the interaction between the Cu atoms. Although we cannot prove that the experimental feature is of local singlet character, the similarity to the theoretical results in terms of weight and energy suggests that this is the case.

In Fig. 2 we compare theoretical results for CuO and Nd_2CuO_4. The shape of the main band differs somewhat due to differences in the hopping matrix elements. The local singlet peak is furthermore slightly weaker for Nd_2CuO_4. The reason is that the hopping matrix elements are somewhat smaller for Nd_2CuO_4. Thus we find that the sum of $|V_{\mathbf{k}m}|^2$ over the occupied states is about 15 % larger for CuO than for Nd_2CuO_4. This leads to less weight in the splitoff states, which is due to hopping. However, the two spectra are quite similar according to the Anderson impurity model, in agreement with common expectations. Figure 2 also shows a calculation for Nd_2CuO_4, where $|V_{\mathbf{k}m}|^2$ has been reduced by a factor 0.6 relative to the calculated value. Even in this case the local singlet has appreciable weight, showing that the calculated hopping matrix elements are substantially larger than is needed in order to obtain a splitoff local singlet state.

In Fig. 2 we finally compare with experimental[4] results for Nd_2CuO_4. Most of the features of the spectra agree rather well. There is, however, a large discrepancy at low binding energies, where theory shows a substantial peak due to the local singlet, while the experiment only shows a very weak structure. This is characteristic for many other high-T_c-related compounds, for which very little or no weight has been observed at the energy where the local singlet is expected. The local singlet could be located at slightly higher binding energies, where it would be hard to see experimentally. This could happen if the highest valence state has little or no coupling to the Cu $x^2 - y^2$ state. The O $2p$ emission (neglected in the calculations) should be larger for Nd_2CuO_4 and may make the local singlet appear smaller for Nd_2CuO_4. We also recall that the ground state has been assumed to have $x^2 - y^2$ symmetry, and that configurations with conduction electrons have been neglected.

It should be noted that the Anderson model is a rather simple model, and that the *ab initio* calculation of the parameters of the model involves uncertainties which are not precisely known. The discrepancy between theory and experiment for Nd_2CuO_4 alone may therefore not seem entirely surprising. It is, however, not very easy to point at a deficiency in the theoretical approach, which is serious for Nd_2CuO_4, but of little importance for CuO. The difference between CuO and Nd_2CuO_4 may provide clues to the electronic structure of high-T_c-related compounds.

One difference between CuO and Nd_2CuO_4 is the long-range geometry. In both cases each Cu atom is surrounded by four O atoms, forming an approximate square. The geometry is different, however, in terms of the more distant neighbors. In Nd_2CuO_4 there are Cu-O-Cu neighbors forming angles of 180°. This means that the Cu atoms can couple relatively efficiently via the O $2p$ orbitals, since both atoms couple strongly to the same $2p$ orbital. In CuO, on the other hand, this angle is

smaller (between 96° and 146°), and the coupling is less efficient. This is illustrated by estimates of the exchange coupling between the Cu spins, which are about a factor of 2 smaller for CuO (Ref. 16) than for La_2CuO_4 (Ref. 17), which has a similar structure to Nd_2CuO_4. This suggests that the neglect of Cu-Cu (indirect) interactions in the Anderson impurity model is a better approximation for CuO than for Nd_2CuO_4. One may therefore expect that dispersion and other broadening effects are more important for Nd_2CuO_4, so that the local singlet may be more broadened and harder to see experimentally. However, it seems questionable if this could fully explain the large difference between CuO and Nd_2CuO_4. Also speaking against this explanation is that a local singlet-related peak in the PES spectrum has been obtained for lattice models[5,6] of La_2CuO_4. One may therefore ask if some interactions or some states not included in these (Anderson-like) models are important for the low-lying excitations in Nd_2CuO_4 but not in CuO.

We have compared theoretical and experimental $3d$ photoemission spectra for CuO and Nd_2CuO_4. The $3d$ spectra of these compounds are expected to be similar because of the presence of formally divalent Cu coordinated to four O atoms. We find satisfactory agreement between theory and experiment, except at small binding energies for Nd_2CuO_4. For CuO theory gives a peak due to the local singlet which agrees rather well with an experimental peak in terms of weight and energy. For Nd_2CuO_4, on the other hand, the local singlet has much more weight than the experimental structures. This suggests that there are important differences between the low-energy excitations for CuO and (undoped) Nd_2CuO_4, which cannot be explained by the Anderson (impurity) model.

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[13] According to our local-density-approximation calculations, the $x^2 - y^2$ $3d$ level is located about 0.4 and 0.7 eV below the highest occupied state for CuO and Nd_2CuO_4, respectively. If we define $4t_{pd}^2 = \sum_{\mathbf{k}}^{\mathrm{occ}} |V_{\mathbf{k}m}|^2$ for $m = x^2 - y^2$, we find that t_{pd} is 1.77 and 1.65 eV for CuO and Nd_2CuO_4, respectively. We further used the parameters $U = 8$ eV, $F^2 = 11.4$ eV, and $F^4 = 7.3$ eV.
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